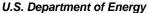# Interim Report on Task 1.4: Impurity Effects Part 1 of 2 To Lawrence Livermore National Laboratory for Contract B345772

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**U.S. Department of Energy**

Lawrence
Livermore
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Laboratory

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# ansto
## materials division

**Interim Report on Task 1.4: Impurity Effects**

**Part 1 of 2**

**To Lawrence Livermore National Laboratory for Contract B345772**

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# Interim Report on Task 1.4: Impurity Effects

# To Lawrence Livermore National Laboratory for Contract B345772

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# 1  SUMMARY

From our work with baseline ceramics containing Pu, or Ce substituted for Pu, doped with sets of inactive impurity ions (with supposedly the same valency) and sintered in different atmospheres, the conclusion is that all ions of similar size and valency are indeed crystal-chemically equivalent unless there are volatility problems. However, the real question appears to be what are the appropriate valency states of the multivalent impurity ions under given sintering conditions. For example, when sintered in highly reducing atmospheres (in this case 3.7 % hydrogen in argon) Mo, W, Zn, Fe, Cu, Co and Ni are reduced to metal.

The partitioning across the different phases present is apparently not even. The elements from the nominal 2+, 3+, 4+, 5+ and 6+ families will preferentially move to certain phases or result in the formation of new phases if sufficient amounts are present. If the phases of the baseline ceramic (pyrochlore-zirconolite, brannerite and rutile) are saturated with these ions, new phases will form to take up the excess impurity ions. Additional such phases detected in this work included ulvospinel, perovskite, magnetoplumbite, loveringite-like phases, metallic alloys and powellite/scheelite.

The Pu and Ce-doped samples give similar results to each other. While samples sintered in air are similar in terms of phases present (with some variations, which are discussed in the text) there are differences in the compositions of the phases.

In summary, the (probably) divalent ions Mn, Fe, Co, Ni, and Mg behave similarly, but certainly Cu, and possibly Zn, show some volatility losses. Al, Ga, Cr, and trivalent Fe, and Mn, all behave similarly to each other, with some minor variations. Hf, Zr and Sn also behave similarly to each other – however, the Sn is converted to the metallic state in reducing atmospheres. Nb and Ta are equivalent. Mo and W behaved equivalently other, but displayed significantly different partitioning ratios into the pyrochlore and scheelite/powellite phases; both reduced to metal in hydrogenous atmospheres. We contend V is pentavalent to at least some extent even in Ar atmospheres and acts as a flux. Of the glass formers Al is not equivalent to B as the Al tends to enter the crystalline phases and promotes the formation of zirconolite, whereas B is a much stronger glass former. Na is not equivalent to K. Addition of Na promotes the formation of a Na-Ce perovskite, when the ceramics are sintered in Ar, and Na enters the pyrochlore, zirconolite and glass. K was only found in the glass. Both K and Na are believed to be partially volatile under the sintering conditions tested.

# 2  INTRODUCTION

## 2.1  Goal of Task 1.4

In the statement of work, the goal of Task 1.4 is:

> "The primary goal for the impurity tests performed at ANSTO is to categorise impurities into categories of equivalence or near equivalence. For example, can Al, Ga, Fe, Cr and V all be treated as a single impurity in the formulation where the sum of the molar quantities of the impurity determines the product properties."

The primary region of confusion with this goal is the definition of the term equivalence: clearly, no two different elements are exactly equivalent. For this work, we have assumed that ionic equivalence means equi-partitioning into the same sites in the various phases of the ceramic.

## 2.2  Strategy Adopted

The strategy adopted to determine this goal has been to initially categorise elements into families based on equivalent valency (Tables 1-5). These families of elements were then added to a baseline ceramic, nominally, 95 wt. % pyrochlore ($Ca_{0.89}Gd_{0.22}$(Pu or Ce)$_{0.22}U_{0.44}Hf_{0.23}Ti_2O_7$) and 5 wt. % rutile, ($Ti_{0.9}Hf_{0.1}O_2$). Note that the actual baseline ceramics usually consist of pyrochlore with 10-20 wt. % brannerite and ~ 5 wt. % rutile and, when impurity elements are present, additional phases such as zirconolite and a glass can form. For the purposes of this work, we shall consider the primary phases to be pyrochlore-zirconolite, rutile and brannerite. The aim was to add a sufficient amount of each of these families of impurity ions[1] so that the primary phases are saturated with them. Hence, secondary phases were expected to form. If the elements in the family partition approximately equally in the phase they can be considered to be equivalent.

For the glass-doped batches, initially a baseline material with ~ 13 wt. % of LLNL glass (B3-13, see Experimental Section below) was made and sintered at 1250, 1300 and 1350°C for 4 hours in Ar. Additional batches were made with excess $B_2O_3$, $Al_2O_3$, $K_2O$ or $Na_2O$. Whereas in the nominally 2+ to 6+ families of impurity ions equivalence is based on crystal-chemical equivalence, whereas with glasses the equivalence can be crystal chemical or physical. For example, two elements A and B may both result in the formation of a glass which contains equivalent amounts of A or B. Compared to B however, A may produce a less viscous glass, which will lower the sintering temperature required and will usually promote grain growth.

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[1] For the 2+ to 6+ families, the total amount added to each batch was ~ 13 wt. % (with some minor

**Table 1: Families of equivalent elements tested.**

| Nominal Ionic Charge | Elements | Expected outcome |
|---|---|---|
| 2+ | Mg, Co, Ni, Cu, Zn | Zirconolite stabiliser[*] |
| 2+ with Mn and Fe | Mg, Co, Ni, Cu, Zn, Mn, Fe | Zirconolite stabiliser[*] |
| 3+ | Al, V, Cr, Mn, Fe, Ga | Zirconolite stabiliser[*] |
| 3+ no V | Al, Cr, Mn, Fe, Ga | Zirconolite stabiliser[*] |
| 4+ | Sn, Zr, Hf | Zirconolite stabiliser [#] |
| 5+ | Nb, Ta | Pyrochlore stabiliser |
| 6+ | Mo, W | Pyrochlore stabiliser |
| 4+ actinides | Th, Np | Pyrochlore stabiliser |
| Glass formers | B, Si, Na, K, Al | Glass former |

* Impurities expected to enter the Ti sites; charge compensation will take place via rare-earth and/or actinide entering the Ca sites to give 2M zirconolite.
# Impurities are expected to enter the Hf-Zr site – progressive addition will drive the pyrochlore to 4M zirconolite and then 2M zirconolite.

# 3 EXPERIMENTAL

In this work a Ce-doped (substituting for Pu) precursor, of the baseline composition, was prepared (Tables 2 and 3). This is designed to give a 95 wt. % pyrochlore, 1 wt. % $HfO_2$ and 4 wt. % $TiO_2$ mixture. On sintering, the hafnia and titania form a solid solution ($Ti_{0.9}Hf_{0.1}O_2$).

## 3.1 Composition and Preparation

### 3.1.1 Pyrochlore and Zirconolite Stabilisers

#### 3.1.1.1 Ce/U-doped samples

Batches of the oxide-basis compositions given in Tables 2 and 3 were prepared by the alkoxide-route using the raw materials given in Tables 4 and 5.

Two precursor batches, each of 100 g, were made. In the first batch (mws980006), the Ca source was calcium hydroxide and the Ce source was cerium nitrate. In the second precursor (mws980069), the Ca source was calcium nitrate and the Ce source was ammonium cerium (IV) nitrate. These batches are given in Table 6.

The precursors were made as follows. The Ti and Hf alkoxides were mixed together and diluted to 50 % by adding anhydrous ethanol. The non-radioactive nitrates/hydroxides (Ca, Gd and Ce) were diluted together in deionised water and added to the alkoxides[2]. This batch was then shear mixed for 10 minutes. It was then taken to the uranium laboratory where uranyl nitrate was added. The sample was stirred and then dried overnight on a hot plate. The dried cake was broken up using a mortar and pestle. A loss on ignition test was performed to determine the oxide content.

Batches of 20 g (oxide basis) were made for each of the equivalent impurity families to be tested. The mixtures were designed to contain equimolar additions of each impurity element, with the exception of: (i) the 2+ with Mn and Fe batch, which contained a lower molar level of Mn and Fe; and (ii) the 4+ batch where the Zr was subsequently found to be deficient by ~ 20 % due to a weighing error[3]. The impurity raw materials (Table 5) were weighed out and mixed with water in a beaker. The required amount of precursor was added to the beaker, which was then placed in an ultrasonic bath for 30 minutes to break up the aggregates. The slurry was stirred for 10 minutes, poured into a stainless steel bowl and dried overnight on a hot plate. The dried cake was lightly ground with a mortar and pestle placed inside an alumina boat and rotary calcined in air for 1 hour at 750°C. The calcined powder was then treated by wet ball milling (water) for 16 hours with zirconia media in a nylon jar. The milled slurry was dried at 110°C.

10 mm diameter and ~ 0.5 g pellets were cold pressed at ~ 90 MPa and then sintered in an alumina tube furnace for 4 hours at 1350°C. The atmospheres used were 0.25 l/min. of Ar,

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[2] Amount of water is 4 times the weight of alkoxide.

air or 3.7% $H_2$ in Ar. The heating and cooling rate was 5°C/min.

An additional 5 g 2+ impurity batch that contained Mn and Fe in addition to the previous elements in the original 2+ batch (Mg, Co, Ni, Cu, Zn), was made by adding Mn and Fe nitrates to the some of original calcine (Table 2). This was mixed together as a slurry, dried, calcined and ball milled as above.

### 3.1.1.2 Th/Np-doped sample

This batch consisted of a mixture of (oxide-basis) 2.00 g of Ce/U-baseline precursor, 0.154 g of $NpO_2$ and 0.149 g of $ThO_2$. The composition is given in Table 7. The precursor was made by the alkoxide-route (Table 6). The Np and Th were added as nitrate solutions. The components were mixed in a 25 ml glass jar, then placed in an ultrasonic bath for 30 min. to break up the agglomerates. Drying was done in a glass beaker on a hot-plate. The dried powder was calcined at 750°C in air for 1 hour in a Pt lined, alumina boat in an alumina tube furnace. The calcined powder was dry-milled for 20 minutes using a MM 2 mixer mill[4] with a zirconia grinding jar and two zirconia balls. Pellets (10 mm dia.) were cold pressed at ~ 90 MPa and sintered at 1350°C in Ar for 4 hours in an alumina tube furnace.

**Table 2: Compositions of the Task 1.4 Ce-doped batches: precursor, and the two nominally 2+ impurity batches.**

| Oxide | Batch | | |
|---|---|---|---|
| | Precursor (Wt. %) | 2+ (Wt. %) | 2+ with Mn and Fe (Wt. %) |
| CaO | 10.43 | 9.07 | 8.84 |
| $CeO_2$ | 7.91 | 6.88 | 6.71 |
| CoO | | 2.79 | 2.72 |
| CuO | | 3.00 | 2.93 |
| FeO | | | 1.30 |
| $Gd_2O_3$ | 8.33 | 7.24 | 7.06 |
| $HfO_2$ | 11.12 | 9.67 | 9.43 |
| MgO | | 1.49 | 1.46 |
| MnO | | | 1.21 |
| NiO | | 2.75 | 2.68 |
| $TiO_2$ | 37.38 | 32.51 | 31.69 |
| $UO_2$ | 24.82 | 21.58 | 21.04 |
| ZnO | | 3.01 | 2.93 |
| Total | 100.00 | 100.00 | 100.00 |

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[4] Model MM 2 Mixer mill, Retsch GmbH, Rheinische Strasse 36, Haan, Germany. Grinding jar used was a 25 ml zirconia jar with cover – Retsch code 01.462.0047. Two 12 mm dia. zirconia balls were used to grind

**Table 3: Compositions of the Task 1.4 Ce-doped batches: precursor, the two nominally 3+, 4+, 5 + and 6+ impurity batches.**

| Oxide | Batch | | | | | |
|---|---|---|---|---|---|---|
| | Precursor (Wt. %) | 3+ (Wt. %) | 3+ no V (Wt. %) | 4+ (Wt. %) | 5+ (Wt. %) | 6+ (Wt. %) |
| $Al_2O_3$ | | 1.46 | 1.51 | | | |
| CaO | 10.43 | 9.08 | 9.27 | 9.15 | 9.07 | 9.08 |
| $CeO_2$ | 7.91 | 6.88 | 7.03 | 6.94 | 6.88 | 6.88 |
| $Cr_2O_3$ | | 2.18 | 2.22 | | | |
| $Fe_2O_3$ | | 2.27 | 2.34 | | | |
| $Ga_2O_3$ | | 2.68 | 2.75 | | | |
| $Gd_2O_3$ | 8.33 | 7.25 | 7.40 | 7.31 | 7.25 | 7.25 |
| $HfO_2$ | 11.12 | 9.68 | 9.88 | 15.50 | 9.67 | 9.68 |
| $Mn_2O_3$ | | 2.25 | 2.35 | | | |
| $MoO_3$ | | | | | | 4.98 |
| $Nb_2O_5$ | | | | | 4.92 | |
| $SnO_2$ | | | | 4.13 | | |
| $Ta_2O_5$ | | | | | 8.09 | |
| $TiO_2$ | 37.38 | 32.53 | 33.21 | 32.80 | 32.52 | 32.53 |
| $UO_2$ | 24.82 | 21.60 | 22.05 | 21.78 | 21.59 | 21.60 |
| $V_2O_3$ | | 2.15 | | | | |
| $WO_3$ | | | | | | 8.01 |
| $ZrO_2$ | | | | 2.39 | | |
| Total | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

**Table 4: Raw materials used for the precursor batches.**

| Element | Raw Materials for Alkoxide-route Batches (raw, material, source, catalogue number) |
|---|---|
| Ca | 99.995 % $Ca(OH)_2$, Aldrich Chem. Co., 45014-6 or |
| | > 99 % $Ca(NO_3)_2.4H_2O$, Aldrich Chem. Co., 23712-4 |
| Ti | Titanium isopropoxide, HÜLS Troisdorf Gmb., 405514 |
| Hf | 99.99 % Hafnium n-butoxide, Gelest Inc. |
| Gd | 99.9 % $Gd(NO_3)_3.6H_2O$, Aldrich Chem., 21159-1 |
| Ce | 99.9 % $Ce(NO_3)_3.6H_2O$, Aldrich Chem., 23853-8 or |
| | > 98.5 % $(NH_4)_2Ce(NO_3)_2$, Aldrich Chem. 43-133-8. |
| Pu | Pu nitrate solution, (Pu-239) made by dissolving $PuO_2$ in 8M $HNO_3$. |
| U | $UO_2(NO_3)_2.6H_2O$, depleted (~ 0.318 % U235), BDH, Batch FF296, 10289 |

**Table 5: Raw materials used for the impurity addition work in Task 1.4.**

| Element | Raw Materials Task 1.4 impurity elements (raw material, source, catalogue number) |
|---------|-----------------------------------------------------------------------------------|
| Mg | > 99 % $Mg(NO_3)_2.6H_2O$, Aldrich Chem., 23717-5 |
| Co | > 99 % $Co(NO_3)_2.6H_2O$, BDH, 100083 |
| Ni | > 99 % $Ni(NO_3)_2.6H_2O$, Fluka, 72253 |
| Cu | > 99 % $Cu(NO_3)_2.3H_2O$, Fluka, 61194 |
| Zn | > 99 % $Zn(NO_3)_2.6H_2O$, Fluka, 96482 |
| Fe | +98 % $Fe(NO_3)_3.9H_2O$, Ajax Chem., Univar 827 |
| Mn | Mn-nitrate solution, BDH, 16658 |
| Al | 99.6 % $Al_2O_3$, Degussa AG, Aluminium Oxide C |
| V | > 99 % $V_2O_3$, Aldrich Chem., 21398-8 |
| Cr | > 99 % $Cr(NO_3)_3.6H_2O$, Fluka, 27080 |
| Ga | 99.9 % $Ga(NO_3)_3.6H_2O$, Aldrich Chem., 28989-2 |
| Zr | Zirconium n-butoxide, HULS Troisdorf GMB., 405537 |
| Sn | 99.9 %, $SnO_2$, -325 mesh, Aldrich Chem., 24465-1 |
| Hf | 99.99 % Hafnium n-butoxide, Gelest Inc. |
| Nb | 99.95 %, $Nb_2O_5$, -325 mesh, Cerac, N-1073 |
| Ta | 99.9 % $Ta_2O_5$, A.D. MacKay Ltd. |
| Mo | $(NH_4)_6Mo_7O_{24}.4H_2O$, May and Baker, L804 |
| W | $(NH_4)_{10}W_{12}O_{41}.5H_2O$, BDH, 27208 |
| Si | Ludox HS-40 colloidal silica, 40% suspension in water, Aldrich Chem., 42081-6 |
| P | 85% $H_3PO_4$, Ajax Chem., |
| B | $H_3BO_3$, Ajax Chem., Unilab 102 |
| K | KOH, Merck, 5033 |
| Na | NaOH, Merck, 6498 |
| Th | $Th(NO_3)_4.5H_2O$, Merck, 1.08162 |
| Np | Np nitrate, (Np-237) AEA Tech. Harwell, 93/237/97 |

**Table 6: Precursors used for Task 1.4 batches; compositions of precursors are given in Tables 2 and 3 above.**

| Nominal Impurity Valency | Precursor used | |
|--------------------------|-----------------|-----------------|
| | **Ce-doped [#]** | **Pu-doped [#]** |
| 2+ | mws980069 | - |
| 2+ with Mn and Fe | mws980069 | 5A |
| 3+ | mws980069 | - |
| 3+ no V | mws980006 | 5A |
| 4+ | mws980069 | 5A |
| 5+ | mws980069 | 5A |
| 6+ | mws980006 | 5A |
| 4+ actinides (Np/Th) | mws980006 | - |
| Glass | mws980006 | - |

# see Tables 2, 3 and 8 for precursor composition.

**Table 7: Compositions of the Task 1.4 Ce-doped batch with Np and Th added.**

| Oxide | Composition (wt. %) |
|-------|------------------|
| CaO | 9.07 |
| CeO$_2$ | 6.88 |
| Gd$_2$O$_3$ | 7.25 |
| HfO$_2$ | 9.67 |
| NpO$_2$ | 6.58 |
| ThO$_2$ | 6.46 |
| TiO$_2$ | 32.51 |
| UO$_2$ | 21.59 |
| Total | 100.00 |

### 3.1.1.3    Pu/U-doped samples

Pu-doped batches (Table 8) containing the nominally 2+, 3+, 4+, 5+ and 6+ impurity families were made using an available Pu-doped, oxide-route precursor. This precursor was chosen because it only contained small amounts of impurities and none of the glass phase formers (B, Si, Na and K). The precursor used was batch 5A (Table 8) made in 1997[5]. The fabrication procedures were the same as those used for the Np/Th doped batch in the preceding section. 10 mm diameter and ~ 0.5 g  pellets were cold pressed at ~ 90 MPa and then sintered in an alumina tube furnace for 4 hours at 1350°C. The atmospheres used were 0.25 l/min of Ar or air. The heating and cooling rate was 5°C/min.

### 3.1.2  Glass Stabilisers

20 g batches of glass stabiliser powders of compositions given in Table 9 were made using the procedure used to make the Ce/U-doped samples in section 3.1.1.1 above.

Pellets from these materials were sintered at 1250, 1300 or 1350°C in Ar.

## 3.2  Analysis

After sintering, the densities of the samples were measured using Archimedes' method, in water for the Ce-doped samples and octanol for the Pu and Np-doped samples, via the evacuation method.

The samples were then mounted in resin and polished to a 0.25-1.0 μm diamond finish. The polished surface was examined by X-ray diffraction (XRD), using either a Siemens D500 diffractometer employing Co K-alpha radiation, or a Scintag  X1 Advanced Diffractometer System, with Cu K-alpha radiation. The samples were examined by scanning electron microscopy (SEM) using either a JEOL JSM6400 or JEOL JSM6300 machines, both of which are fitted with energy dispersive x-ray spectrometry (EDS) instruments for quantitative analysis.

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[5] E.R. Vance, M.W.A. Stewart, R.A. Day, K.P. Hart, M.J. Hambley and A. Brownscombe, *Pyrochlore-rich Titanate Ceramics for Incorporation of Plutonium, Uranium and Process Chemicals*, ANSTO Report,

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**Table 8: Compositions of the Task 1.4 Pu-doped batches containing the nominal impurity valency (wt. %).**

| Oxide * | Batch Precursor 5A (Wt. %) | Batch 2+ (Wt. %) | Oxide # | Batch Precursor 5A (Wt. %) | Batch 3+ (Wt. %) | Batch 4+ (Wt. %) | Batch 5+ (Wt. %) | Batch 6+ (Wt. %) |
|---|---|---|---|---|---|---|---|---|
| $Al_2O_3$ | 0.11 | 0.09 | $Al_2O_3$ | 0.11 | 1.45 | 0.10 | 0.09 | 0.09 |
| CaO | 9.85 | 8.17 | CaO | 9.85 | 8.84 | 8.86 | 8.59 | 8.59 |
| CoO | | 2.61 | CoO | | | | | |
| $Cr_2O_3$ | | | $Cr_2O_3$ | | 1.92 | | | |
| CuO | | 2.76 | CuO | | | | | |
| FeO | 0.14 | 2.58 | $Fe_2O_3$ | 0.16 | 2.30 | 0.14 | 0.14 | 0.14 |
| $Ga_2O_3$ | | | $Ga_2O_3$ | | 2.53 | | | |
| $Gd_2O_3$ | 7.87 | 6.53 | $Gd_2O_3$ | 7.87 | 7.06 | 7.08 | 6.86 | 6.86 |
| $HfO_2$ | 10.54 | 8.75 | $HfO_2$ | 10.54 | 9.46 | 15.41 | 9.19 | 9.19 |
| MgO | 0.46 | 1.77 | MgO | 0.46 | 0.41 | 0.41 | 0.40 | 0.40 |
| MnO | | 2.42 | $Mn_2O_3$ | | 2.24 | | | |
| $MoO_3$ | 0.30 | 0.25 | $MoO_3$ | 0.33 | 0.30 | 0.30 | 0.29 | 5.26 |
| $Nb_2O_5$ | | | $Nb_2O_5$ | | | | 4.74 | |
| NiO | | 2.59 | NiO | | | | | |
| $PuO_2$ | 11.77 | 9.76 | $PuO_2$ | 11.77 | 10.57 | 10.58 | 10.26 | 10.27 |
| $SnO_2$ | | | $SnO_2$ | | | 4.12 | | |
| $Ta_2O_5$ | | | $Ta_2O_5$ | | | | 8.02 | |
| $TiO_2$ | 35.50 | 29.45 | $TiO_2$ | 35.48 | 31.86 | 31.92 | 30.96 | 30.96 |
| $UO_2$ | 23.45 | 19.45 | $UO_2$ | 23.44 | 21.05 | 21.09 | 20.45 | 20.45 |
| $WO_3$ | | | $WO_3$ | | | | | 7.78 |
| ZnO | | 2.83 | ZnO | | | | | |
| $ZrO_2$ | | | $ZrO_2$ | | | 3.44 | | |
| Total | 100.00 | 100.00 | Total | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

* Mn and Fe at 2+ valency state

# Mn and Fe at 3+ valency state

**Table 9: Composition of the glass-doped material. Three grams of this composition was added to 20 g (oxide basis) of the baseline Ce/U-doped precursor.**

| Batch No. | mws980209 | mws980368 | mws980369 | mws980370 |
|---|---|---|---|---|
| | Baseline Precursor + 13 wt. % B3-13 | Additional $Al_2O_3$ | Additional $B_2O_3$ | Additional $Na_2O$ & $K_2O$ |
| Oxide | Wt. % Oxide | Wt. % Oxide | Wt. % Oxide | Wt. % Oxide |
| CaO | 10.79 | 10.28 | 10.41 | 10.28 |
| $Gd_2O_3$ | 7.41 | 7.05 | 7.14 | 7.05 |
| $HfO_2$ | 9.85 | 9.38 | 9.50 | 9.38 |
| $UO_2$ | 21.95 | 20.90 | 21.17 | 20.91 |
| $CeO_2$ | 7.07 | 6.73 | 6.82 | 6.74 |
| $TiO_2$ | 33.59 | 31.97 | 32.40 | 31.99 |
| $Al_2O_3$ | 2.60 | 7.30 | 2.50 | 2.48 |
| MgO | 0.17 | 0.17 | 0.16 | 0.17 |
| $Ga_2O_3$ | 0.24 | 0.23 | 0.23 | 0.23 |
| $Fe_2O_3$ | 0.05 | 0.05 | 0.05 | 0.05 |
| $K_2O$ | 0.09 | 0.08 | 0.08 | 2.94 |
| $Na_2O$ | 0.43 | 0.41 | 0.41 | 2.31 |
| $MoO_2$ | 0.06 | 0.05 | 0.06 | 0.05 |
| $SiO_2$ | 4.62 | 4.40 | 4.46 | 4.40 |
| $B_2O_3$ | 0.71 | 0.67 | 4.24 | 0.68 |
| $P_2O_5$ | 0.35 | 0.33 | 0.33 | 0.33 |
| | | | | |
| Total | 100.00 | 100.00 | 100.00 | 100.00 |

# 4  RESULTS AND DISCUSSION

## 4.1  Pyrochlore and Zirconolite Stabilisers Sintered in Ar

As discussed earlier, the addition of  ~ 13 wt. % of  the nominally 2+ to 6 + impurity families was chosen so that each element was present at detectable levels for the SEM/EDS system and the impurity elements were present in sufficient amounts to saturate the baseline phases, resulting in the formation of new phases.

The SEM micrographs and EDS data have been placed in separate Appendices.  SEM results are given in Appendices A – D; the X-ray diffraction results are given in Appendix E; and the EDS results are in Appendix F.

### 4.1.1  Ce/U-doped Samples Sintered at 1350°C

Densities of the Ce-doped samples are given in Table 10.

#### 4.1.1.1    Nominally 2+ impurities batch (Mg, Co, Ni, Cu, Zn)

The SEM/EDS analysis (Appendix A, Fig. A-1/Appendix F, Table F-1) show that this sample consists of

- pyrochlore
- ~ 15 - 20 vol. % of what is believed to be 2M zirconolite
- ~ 7 - 10 vol. % ulvospinel
- ~ 5 vol. % perovskite

The pellet is deficient in Cu - it was only detected in the ulvospinel, at levels below those of the other nominally 2+ elements (see Table F-1). Under the sintering conditions ($pO_2$ ~ $10^{-5}$ atm.) CuO could be reduced to Cu metal; however metallic Cu was not detected in the microstructure and it may have volatilised, or flowed out of the sample. This is possible because the Cu would be molten at the sintering temperature, if it was metallic.

The sample may also be deficient in Zn (see Table F-1).

The pyrochlore contains small (~ 0.03 – 0.08 formula units) amounts of Mg, Co and Ni. The zirconolite, which we believe to be 2M, contains ~ 0.06 - 0.18 formula units of Mg, Co, Ni and Zn (Table F-1). The perovskite contains Gd and Ce, and a trace of U and Hf plus ~ 0.015 - 0.03 formula units each of Co, Ni and Cu.  Ce, U and Gd were not detected in the ulvospinel, which contained all the added nominally 2+ impurity elements, plus a trace of Fe and Cr from processing contaminants. The Cu in the ulvospinel is deficient relative to the rest of the nominally 2+ impurity elements.

**Table 10: Densities of the Task 1.4 samples made from the Ce/U-doped precursor. Pellets were prepared by sintering for 4 hours at 1350°C in Ar, air or 3.7% $H_2$ in Ar.**

| Pellet No. | Powder Batch No. | Description | Sintering Atm. | Archimedes Density (g/cm$^3$) | Open Porosity (%) |
|---|---|---|---|---|---|
| mws980041 | mw980006 | Precursor mw980006 | Ar | 5.10 | 4.1 |
| mws980042 | mw980006 | Precursor mw980006 | Ar | 5.10 | 3.3 |
| mws980070 | mws980069 | Precursor mws980069 | Ar | 4.82 | 3.3 |
| | | | | | |
| mws980087 | mws980077 | 2+  Mg, Co, Ni, Cu, Zn | Ar | 5.09 | 0.4 |
| mws980088 | mws980077 | 2+  Mg, Co, Ni, Cu, Zn | Ar | 4.95 | 0.5 |
| | | | | | |
| mws980224 | mws980207 | 2+  Mg, Co, Ni, Cu, Zn, Mn, Fe | Ar | 4.74 | 3.1 |
| mws980226 | mws980207 | 2+  Mg, Co, Ni, Cu, Zn, Mn, Fe | air | melted | |
| mws980336 | mws980207 | 2+  Mg, Co, Ni, Cu, Zn, Mn, Fe | 3.7%$H_2$/Ar | 5.41 | 6.5 |
| | | | | | |
| mws980089 | mws980078 | 3+  Al, V, Cr, Mn, Fe, Ga | Ar | 5.18 | 1.8 |
| mws980090 | mws980078 | 3+  Al, V, Cr, Mn, Fe, Ga | Ar | 5.08 | 7.2 |
| | | | | | |
| mws980224 | mws980208 | 3+  Al, Cr, Mn, Fe, Ga | Ar | 4.10 | 1.8 |
| mws980226 | mws980208 | 3+  Al, Cr, Mn, Fe, Ga | air | 4.09 | 3.0 |
| mws980337 | mws980208 | 3+  Al, Cr, Mn, Fe, Ga | 3.7%$H_2$/Ar | 4.64 | 3.2 |
| | | | | | |
| mws980091 | mws980079 | 4+  Sn, Zr, Hf | Ar | 4.81 | 0.3 |
| mws980092 | mws980079 | 4+  Sn, Zr, Hf | Ar | 4.52 | 0.4 |
| mws980201 | mws980079 | 4+  Sn, Zr, Hf | air | 3.87 | 11.0 |
| mws980204 | mws980079 | 4+  Sn, Zr, Hf | 3.7%$H_2$/Ar | 5.43 | 3.4 |
| | | | | | |
| mws980093 | mws980080 | 5+  Nb, Ta | Ar | 5.36 | -0.6 |
| mws980094 | mws980080 | 5+  Nb, Ta | Ar | 5.25 | 0.2 |
| mws980131 | mws980130 | 5+  Nb, Ta | Ar | 5.38 | 0.8 |
| mws980132 | mws980130 | 5+  Nb, Ta | Ar | 5.40 | 1.3 |
| mws980202 | mws980130 | 5+  Nb, Ta | air | 5.38 | 1.6 |
| mws980205 | mws980130 | 5+  Nb, Ta | 3.7%$H_2$/Ar | 5.61 | 2.1 |
| mws980290 | mws980130 | 5+  Nb, Ta | 3.7%$H_2$/Ar | 5.15 | 9.7 |
| | | | | | |
| mws980095 | mws980081 | 6+  Mo, W | Ar | 4.87 | 11.2 |
| mws980096 | mws980081 | 6+  Mo, W | Ar | 4.91 | 8.9 |
| mws980203 | mws980081 | 6+  Mo, W | air | 5.37 | 0.0 |
| mws980206 | mws980081 | 6+  Mo, W | 3.7%$H_2$/Ar | 5.79 | 3.3 |
| mws980291 | mws980081 | 6+  Mo, W | 3.7%$H_2$/Ar | 5.64 | 5.7 |

### 4.1.1.2 Nominally 2+ impurities batch with Mn and Fe (Mg, Co, Ni, Cu, Zn, Fe, Mn)

The SEM/EDS analysis (Appendix A, Fig. A-2/Appendix F Table F-2) show that this sample consists of:

- pyrochlore, which exhibits some compositional zoning
- ~ 15-20 vol. % of what is believed to be 2M zirconolite
- ~ 10 vol. % ulvospinel
- ~ 5 vol. % perovskite

The results are generally similar to that of the above mentioned nominally 2+ impurity sample without Fe and Mn (section 4.1.1.1). The pyrochlore contains small (~ 0.03 – 0.08 formula units) amounts of Fe, Mn, Mg, Co and Ni (Table F-2).  The zirconolite contains ~ 0.04 - 0.16 formula units each of Fe, Mn, Mg, Co, Ni and Zn (Table F-2). The perovskite again contains Gd and Ce plus a trace of U and Hf. The Ce believed to be in the 3+ state in the perovskite, though further work, such as XANES,  would need to be done to confirm this. The perovskite also contains a small amount (~ 0.005 - 0.03 formula units each) of Mn, Fe, Co, Ni and Cu. The ulvospinel contains all the added elements plus a trace of impurity Cr. The Mn is slightly deficient in the ulvospinel.

### 4.1.1.3 Nominally 3+ impurities batch with V (Al, V, Cr, Mn, Fe, Ga)

The SEM/EDS analysis (Appendix A, fig. A-3/ Appendix F, Table F-3) show that this sample consists of:

- pyrochlore
- ~ 30 vol. % of what is believed to be 2M zirconolite
- ~ 10 vol. % of a titanate phase, possibly loveringite

The zirconolite is believed to be the 2M polytype, from the X-ray pattern.  This is expected from the relatively large impurity doping of 3d elements in the Ti sites, which necessitates charge compensation by Ce, U and Gd substituting for Ca in the Ca site.

Approximately 0.38 formula units in total of the nominally 3+ family of elements enter the pyrochlore. The elements partition approximately equivalently in the pyrochlore apart from Mn, which is present in a slightly higher quantity. The Fe, V, Cr, Ga, Mn and Al are present in approximately equivalent amounts in the zirconolite. About 0.7 formula units in total of the family of nominally 3+ elements enter the zirconolite. The V is deficient in the zirconolite. The "loveringite-like" phase contains approximately equivalent amounts of Cr, Ga, Al and Fe, slightly less V and Mn.  Hence, V appears to be deficient in the sample.

The pellet has rounded grains (fig. A-3) and we believe this indicates localised melting. Vanadium is likely to exist as $V^{5+}$ (vanadate), even under an argon atmosphere.  Such metal vanadates are often used as a crystal growth flux at ~ 1200_C. This does not preclude the existence of trivalent V as V is incorporated into the pyrochlore and zirconolite.

The existence of Fe and Mn at 2+ valency is a distinct possibility under the sintering conditions used.

From the above results the Al, Cr, Mn, Fe and Ga can be considered equivalent. This is because all of these elements can be nearly equally accommodated into the pyrochlore and zirconolite. The equivalence of V (as $V^{3+}$) is debatable. At the relatively large amounts used in this study, V induces melting, however, significant amounts are still incorporated into the pyrochlore and zirconolite, which probably indicates that $V^{3+}$ is equivalent to the other 3+ elements.

In view of the complications attributed to the use of V, we repeated the experiment without V.

### 4.1.1.4    Nominally 3+ impurities batch without V (Al, Cr, Mn, Fe, Ga)

The SEM/EDS analysis (Appendix A, fig. A-4/ Appendix F, Table F-4) show that this sample consists of:

- pyrochlore
- ~ 30 vol. % of what is believed to be 2M zirconolite
- ~ 5 - 10 vol. % perovskite
- ~ 5 - 10 vol. % of a titanate phase, probably loveringite

The sample has a different microstructure to that of the V-doped batch above (section 4.1.1.3), in so far as it is more porous, contains a perovskite phase, and no liquid-phase sintering was apparent - in agreement with the idea expressed in section 4.1.1.3 that V resulted in local melting.

Approximately 0.31 formula units of the 3+ family of elements enter the pyrochlore. The elements partition approximately equivalently within the pyrochlore, apart from Mn, which is present in a slightly higher quantity. The Fe, Cr, Ga, Mn and Al are present in approximately equivalent amounts in the zirconolite; about 0.7 formula units of the family of nominally 3+ elements enter the zirconolite. The perovskite contains approximately equal amounts of Al, Ga, Cr and Fe. The Mn and Fe are relatively deficient in the perovskite. The "loveringite-like" phase contains approximately equivalent amounts of Cr and Fe, slightly less Ga and Al, and significantly less Mn.

### 4.1.1.5    Nominally 4+ impurities batch (Zr, Sn, Hf)

The SEM/EDS analysis (Appendix A, fig. A-5/Appendix F, Table F-5) show that this sample consists of

- pyrochlore
- ~ 25  vol. % 4M zirconolite
- ~ 25 vol. % 2M zirconolite
- ~ 7 - 10 vol. % brannerite
- ~ 5 vol. % rutile
- ~ 2 - 5  vol. % hafnium titanate $((Hf,Zr,Sn)TiO_4)$

The main effect of Zr, Hf and Sn additions is to promote zirconolite formation at the expense of pyrochlore. Hafnium titanate also forms.  Approximately equivalent amounts of Sn, Zr and Hf can be found in the zirconolites, pyrochlore, hafnium titanate and rutile, with some minor variations, namely, that the Sn has a greater tendency to enter the pyrochlore and 4M zirconolite than Hf or Zr. No Sn was detected in the brannerite.

### 4.1.1.6　　Nominally 5+ impurities batch (Nb, Ta)

The SEM/EDS analysis (Appendix A, fig. A-6/Appendix F Table F-6) show that this sample consists of:

- Pyrochlore
- ~ 10 vol. % brannerite
- ~ 10 vol. % rutile

Approximately 0.5 formula units of Nb + Ta enter the pyrochlore in the Ti site (i.e., ~ 25 % of the Ti sites are occupied by Ta or Nb in this batch). The rutile contains ~ 0.07 formula units of Nb + Ta and the brannerite ~ 0.14 formula units of Nb + Ta; i.e., ~ 7 % of the Ti sites in these phases are occupied by Ta + Nb. No zirconolite formed. The Nb and Ta evidently prefer to enter the pyrochlore. The Nb and Ta enter each phase in approximately equivalent amounts.

### 4.1.1.7　　Nominally 6+ impurities batch (Mo, W)

The SEM/EDS analysis (Appendix A, fig. A-7/Appendix F, Table F-7) show that this sample consists of:

- Pyrochlore
- ~ 20-25 vol. % brannerite
- ~ 5 vol. % rutile
- ~ 10 vol. % of a $Ca(W,Mo)O_4$ (scheelite/powellite) solid solution

Little, if any, Mo and W enter the brannerite or rutile. About 2-3 times as much W as Mo enters the pyrochlore. The total W and Mo in the pyrochlore is ~ 0.2 formula units. The $Ca(W,Mo)O_4$ contains about twice as much Mo as W. The presence of W and Mo above the solubility limits in pyrochlore has sequestered Ca, leading to more brannerite formation.

## 4.1.2　Pu/U-doped Samples Sintered in Ar at 1350°C

Densities of the pellets are given in Table 11.

### 4.1.2.1　　Nominally 2+ impurities batch with Mn and Fe (Mg, Co, Ni, Cu, Zn, Fe, Mn)

The SEM/EDS analysis (Appendix A, fig. A-8/Appendix F, Table F-8) show that this sample consists of:

- Pyrochlore which exhibits some zoning (fig. A-8)
- ~ 10 vol. % ulvospinel

The microstructure is different to the equivalent Ce/U-doped batch (section 4.1.1.2 above) in that 2M zirconolite and perovskite were not detected in the microstructure and the grain size was slightly larger. In addition, Ni was not detected in the pyrochlore, whereas it was detected in small amounts in the Ce/U-doped pyrochlore. The pyrochlore contains a similar amount of nominally 2+ impurities to the Ce/U-doped batch (~ 0.3 formula units).

**Table 11 Densities of Pu/U-doped assemblage/impurity solubility samples sintered**

**for Task 1.4. Pellets were prepared by sintering for 4 hours at 1350°C in Ar or air.**

| Pellet No. | Description | Sintering Atm. | Archimedes Density (g/cm$^3$) | Open Porosity (%) |
|---|---|---|---|---|
| Pu107-01 | 2+  Mg, Co, Ni, Cu, Zn, Mn, Fe | Ar | 5.21 | 0.6 |
| Pu107-02 | 2+  Mg, Co, Ni, Cu, Zn, Mn, Fe | air | 4.94 | 1.5 |
| | | | | |
| Pu108-01 | 3+  Al, Cr, Mn, Fe, Ga | Ar | 5.28 | 0.3 |
| Pu108-02 | 3+  Al, Cr, Mn, Fe, Ga | air | 5.25 | 0.1 |
| | | | | |
| Pu109-01 | 4+  Sn, Zr, Hf | Ar | 5.80 | 0.1 |
| Pu109-02 | 4+  Sn, Zr, Hf | air | 5.81 | 0.1 |
| | | | | |
| Pu110-01 | 5+  Nb, Ta | Ar | 5.63 | 0.04 |
| Pu110-02 | 5+  Nb, Ta | air | 5.64 | 0.07 |
| | | | | |
| Pu111-01 | 6+  Mo, W | Ar | 5.55 | 0 |
| Pu111-02 | 6+  Mo, W | air | 5.24 | 1.3 |

### 4.1.2.2    Nominally 3+ impurities batch without V (Al, Cr, Mn, Fe, Ga)

The SEM/EDS analysis (Appendix A, fig. A-9/Appendix F, Table F-9) show that this sample consists of:

- pyrochlore
- ~ 25 vol. % 2M zirconolite
- ~ 5 vol. % of what is believed to be magnetoplumbite
- ~ 5 vol. % of what is probably a loveringite type phase

The distribution of the nominally 3+ elements is not exactly uniform. Al and Ga do not enter the pyrochlore in detectable amounts. Mn is present in similar amounts in the pyrochlore and 4M zirconolite. There is slightly more Fe and Cr in the 2M zirconolite than the pyrochlore. The Mg impurity in the precursor powder concentrates in magnetoplumbite and loveringite. Mg was not detectable in the pyrochlore and zirconolite. Pu and U are present in the pyrochlore, zirconolite and loveringite. All the phases contain neutron poison Gd and/or Hf, though Gd was not detectable in the loveringite.

The structure is different to the Ce/U-doped samples ( section 4.1.1.4 above) in that it was less porous and did not contain perovskite. The Ce/U batch did not contain magnetoplumbite.  However, the amount of the 3+ elements in the pyrochlore (~ 0.3 formula units) and zirconolite (~ 0.7 formula units) is similar to the Ce/U-doped sample.

### 4.1.2.3    Nominally 4+ impurities batch (Zr, Sn, Hf)

The SEM/EDS analysis (Appendix A, fig. A-10/Appendix F, Table F-10) show that this sample consists of:

- pyrochlore
- ~ 30 - 40 vol. % of what is believed to be 2M zirconolite
- ~ 10 vol. % brannerite
- ~ 10 vol. % hafnium titanate ($(Hf,Zr,Sn)TiO_4$)
- ~ 2-3 vol. % rutile

- $\ll$ 1 vol. % $(Pu,U)O_2$

The partitioning of the Sn, Hf and Zr is approximately equivalent except that little if any, Sn enters the brannerite and the rutile appears to be slightly enriched in Hf with respect to Zr and Sn. The results are similar to the equivalent Ce/U-doped batch (section 4.1.1.5).

### 4.1.2.4　Nominally 5+ impurities batch (Nb, Ta)

The SEM/EDS analysis (Appendix A, fig. A-11/Appendix F, Table F-11) show that this sample consists of:

- pyrochlore
- ~ 10-15 vol. % rutile.
- ~ 10 vol. % brannerite.
- $\ll$ 1 vol. % $(Pu,U)O_2$

The Nb and Ta are present in equivalent amounts in each phase. The Nb and Ta preferentially enter the pyrochlore.

The results are similar to the Ce/U-doped batches (section 4.1.1.6).

### 4.1.2.5　Nominally 6+ impurities batch (Mo, W)

The SEM/EDS analysis (Appendix A, fig. A-12/Appendix F, Table F-12) show that this sample consists of:

- pyrochlore.
- ~ 20 vol. % brannerite.
- ~ 5 vol. % rutile
- ~ 7 - 10 vol. % scheelite/powellite $(Ca(W,Mo)O_4)$

There are only small amounts of Mo and W in the brannerite or rutile. About 3 times as much W as Mo enters the pyrochlore, on a molar basis. The $Ca(W,Mo)O_4$ contains about twice as much Mo as W.

The results are similar to the Ce/U-doped batches (section 4.1.1.7).

## 4.1.3　Th/Np-doped Batches.

The SEM/EDS analysis (Appendix A, fig. A-13/Appendix F, Table F-13) show that this sample consists of:

- pyrochlore
- ~ 15 vol. % Ce/Th/U/Np-brannerite.
- $(Gd,Ce,Th,Np,U)O_2$ (~ 1-2 vol. %), which contains equivalent amounts of Th and Np. The composition of this oxide is ~ $Ca_{0.05}Gd_{0.11}Ce_{0.13}Np_{0.13}Th_{0.13}U_{0.50}Hf_{0.02}Ti_{0.01}O_2$

The addition of approximately 15 wt. % combined oxides of Th and Np to the baseline has saturated the system, consuming the excess Hf-doped rutile. A mixed Gd-Ce-Th-U-Np oxide forms from the rare-earth/actinide elements that are not incorporated in the pyrochlore or brannerite.

The Th tends to be enriched in the brannerite phase and deficient in the pyrochlore, relative to the Np. The Th and Np partition equivalently in the actinide/rare earth oxide that

## 4.2  Sintering Atmosphere Effects on Pyrochlore and Zirconolite Stabilisers

### 4.2.1  Sintering Ce/U-doped Samples in Air

Densities of the Ce/U-doped pellets are given in Table 10.

#### 4.2.1.1     Nominally 2+ impurities batch (Mg, Co, Ni, Cu, Zn, Fe, Mn)

This sample showed local melting and was very porous (up to ~ 1 mm diameter pores), but it had regions of low porosity between the pores.

The SEM/EDS analysis (Appendix B, Fig. B-1/Appendix F, Table F-2) show that this sample consists of:

* pyrochlore
* ~ 15 - 20 vol. % of  2M zirconolite
* ~ 15 vol. % ulvospinel

The results are similar to the nominally 2+ impurity batch sintered in Ar (section 4.1.1.2) except that no perovskite was detected and the composition of the pyrochlore is different – it contains more Ca (Table F-2).  The pyrochlore contained Fe, Mn, Mg and Co and the zirconolite contained Fe, Mn, Mg, Co, Ni and Zn in detectable amounts. The ulvospinel contains all the added elements and a trace of Cr. The Mn is slightly deficient in the ulvospinel.

In this sample, we would expect iron to be trivalent. In the EDS analysis, the Mn has been assumed to be trivalent, though it could be in the 4+ state.

#### 4.2.1.2     Nominally 3+ impurities batch (Al, Cr, Mn, Fe, Ga)

The SEM/EDS analysis (Appendix B, fig. B-2/Appendix F, Table F-4) show that this sample consists of:

* pyrochlore
* ~ 30 - 40 vol. % of what is believed to be 2M zirconolite
* ~ 10 vol. % of a titanate phase, which is probably a loveringite

The results are similar to the 3+ batch sintered in Ar (section 4.1.1.2) except that no perovskite was detected and the pyrochlore contains more Ca (Table F-4), which changes the overall composition slightly. The nominally 3+ family of elements enter the pyrochlore. These elements partition approximately equivalently within the pyrochlore, with the exception of Mn, which is present in a slightly higher quantity. The Fe, Cr, Ga, Mn and Al are present in approximately equivalent amounts in the zirconolite . The "loveringite-like" phase contains approximately equivalent amounts of the 3+ elements, except for Mn, which is slightly deficient with respect to the other nominally 3+ elements.

### 4.2.1.3     Nominally 4+ impurities batch (Zr, Sn, Hf)

The SEM/EDS analysis (Appendix B, fig. B-3/Appendix F, Table F-5) show that this sample consists of

- pyrochlore
- ~ 15 vol. % 2M zirconolite
- ~ 15 vol. % hafnium titanate ($(Hf,Zr,Sn)TiO_4$)
- ~ 5 vol. % rutile

Approximately equivalent amounts of Sn, Zr and Hf can be found in the pyrochlore, zirconolite, hafnium titanate and rutile, with some minor variations, namely, that the Sn has a greater tendency to enter the pyrochlore than the zirconolite. No brannerite was detected.

The results are different to the Ar sinters (section 4.1.1.5) in that no brannerite was detected and the pyrochlore composition is different.

### 4.2.1.4     Nominally 5+ impurities batch (Nb, Ta)

The SEM/EDS analysis (Appendix B, fig. B-4/Appendix F, Table F-6) show that this sample consists of:

- pyrochlore
- ~ 20 vol. % rutile

The Nb and Ta prefer to enter the pyrochlore. Some Nb and Ta also enter the rutile. The Nb and Ta enter each phase in approximately equal amounts, to each other. Like the 4+ batch above (section 4.2.1.3). The major difference to the Ar sinters (section 4.1.1.6) is that no brannerite was detected.

### 4.2.1.5     Nominally 6+ impurities batch (Mo, W)

The SEM/EDS analysis (Appendix A, fig. B-5/Appendix F, Table F-7) show that this sample consists of:

- Pyrochlore
- ~ 25 vol. % brannerite
- ~ 5 vol. % rutile
- ~ 10 vol. % of a $Ca(W,Mo)O_4$ (scheelite/powellite) solid solution

The results are the similar to the Ar sintered pellet (section 4.1.1.7, above) Little, if any, Mo and W enter the brannerite or rutile. About 2 to 3 times as much W as Mo enters the pyrochlore. The total W and Mo in the pyrochlore is ~ 0.2 formula units The $Ca(W,Mo)O_4$ contains about twice as much Mo as W.

The pyrochlore has more Ca than the Ar sinter (Table F-7)

## 4.2.2  Sintering Pu/U-doped Samples in Air

Densities of the Pu/U-doped pellets are given in Table 10.

### 4.2.2.1 Nominally 2+ impurities batch (Mg, Co, Ni, Cu, Zn, Fe, Mn)

The SEM/EDS analysis (Appendix B, Fig. B-6/Appendix F, Table F-8) show that this sample consists of:

- pyrochlore, with some compositional zoning
- ~ 15 - 20 vol. % of 2M zirconolite
- ~ 10 - 15 vol. % ulvospinel

The results are similar to the nominally 2+ impurity batch Ce/U sintered in air (section 4.1.2.1) except that the composition of the pyrochlore is different – it contains more Ca (Table F-8). The pyrochlore contained Fe, Mn, Mg and Co and the zirconolite contained Fe, Mn, Mg, Co and Ni, in detectable amounts. The ulvospinel contains all the added elements and a trace of Cr. The Mn is slightly deficient in the ulvospinel. Zn was only detected in the ulvospinel. There is more Cu and Zn in the sample than in the Ar sintered sample (Table F-8).

### 4.2.2.2 Nominally 3+ impurities batch (Al, Cr, Mn, Fe, Ga)

The SEM/EDS analysis (Appendix B, fig. B-7/Appendix F, Table F-10) show that this sample consists of:

- pyrochlore
- ~ 30 - 40 vol. % of 2M zirconolite
- ~ 10 vol. % of a loveringite-like phase
- < 1 vol. % brannerite
- < 1 vol. % $(Pu,U)O_2$

The nominally 3+ Al, Cr, Mn and Fe were detected in the pyrochlore. These elements partition approximately equivalently within the pyrochlore, with the exception of Mn, which is present in a slightly higher quantity. All the 3 + elements are present in approximately equivalent amounts in the zirconolite, except for Ga , which is enriched. The loveringite contains approximately equivalent amounts of the 3+ elements, except for Mn, which is slightly deficient, with respect to the other 3+ elements. Very small amounts (< 1 vol. %) of brannerite and $(Pu,U)O_2$ are present. The latter may have precipitated out of solution since it contains significant amounts of Ca and Gd as well as some Hf and Ti (Table F-9).

The results are similar to the Ar sinter (section 4.1.2.3) except that no magnetoplumbite was detected in this sample. As with the Ar sinter the main effect of the nominally 3+ elements has been to promote zirconolite formation at the expense of pyrochlore, with loveringite forming from the remaining 3+ impurity elements.

### 4.2.2.3 Nominally 4+ impurities batch (Zr, Sn, Hf)

The SEM/EDS analysis (Appendix B, fig. B-8/Appendix F, Table F-10) show that this sample consists of

- pyrochlore
- ~ 15 vol. % hafnium titanate $((Hf,Zr,Sn)TiO_4)$
- ~ 5 vol. % 2M zirconolite
- ~ 3 - 5 vol. % rutile

- $\ll 1$ vol. % $(Pu,U)O_2$

Approximately equivalent amounts of Sn, Zr and Hf can be found in the pyrochlore, zirconolites, hafnium titanate, brannerite and rutile, with some minor variations, namely, that the Sn has a greater tendency to enter the pyrochlore than Hf or Zr.

### 4.2.2.4    Nominally 5+ impurities batch (Nb, Ta)

The SEM/EDS analysis (Appendix B, fig. B-9/Appendix F, Table F-11) show that this sample consists of:

- pyrochlore
- ~ 10 – 15 vol. % brannerite
- ~ 15 vol. % rutile
- $\ll 1$ vol. % $(Pu,U)O_2$

The results are similar to the Ar sintered batch (section 4.1.2.4). Nb and Ta prefer to enter the pyrochlore. Some Nb and Ta also enter the brannerite and rutile. The Nb and Ta enter each phase in approximately equal amounts, to each other. Like the 4+ batch above (section 4.2.2.3) the major difference to the Ar sinters (section 4.1.1.5) is that no brannerite was detected and the pyrochlore composition is different.

### 4.2.2.5    Nominally 6+ impurities batch (Mo, W)

The SEM/EDS analysis (Appendix A, fig. B-10/Appendix F, Table F-12) show that this sample consists of:

- pyrochlore
- ~ 25 vol. % brannerite
- ~ 5 vol. % rutile
- ~ 10 vol. % of a $Ca(W,Mo)O_4$ (scheelite/powellite) solid solution

The results are the similar to the Ar sintered pellet (section 4.1.2.5). Little, if any, Mo and W enter the brannerite or rutile. About 2 - 3 times as much W as Mo enters the pyrochlore. The total W and Mo in the pyrochlore is ~ 0.2 formula units. The $Ca(W,Mo)O_4$ contains about twice as much Mo as W.

The pyrochlore has slightly more Ca than the Ar sinter (Table F-7)

As with the Ar sinter, the excess W and Mo forms powellite/scheelite. This has the effect of using up Ca from the system, which results in an increase in the amount of  brannerite.

### 4.2.3  Sintering Ce/U-doped Samples in  3.7 % H$_2$ in Ar

Densities of the Ce/U-doped pellets are given in Table 10.

#### 4.2.3.1    Nominally 2+ impurities batch (Mg, Co, Ni, Cu, Zn, Fe, Mn)

The SEM/EDS analysis (Appendix C, Fig. C-1/Appendix F, Table F-2) show that this sample consists of:

- 4M zirconolite
- ~ 25 vol. % perovskite
- ~ 5 - 10 vol. % of metallic alloys of variable composition (Co-Ni-Cu-Fe)
- ~ 7 vol. % of an unidentified magnesium titanate phase (Mg-Hf-Ti-O, which contains a trace of Ca, Al, Mn and U).

The main phase has a different composition (Table F-2) to the pyrochlore in the Ar and air samples, and is believed to be 4M zirconolite. The composition of the main phase suggests that this phase lies close to the 4M zirconolite – pyrochlore boundary. This compositional change is probably due to Ti$^{3+}$ formation. The 4M zirconolite contains some Mg and Mn, but the other impurities were not detected. The perovskite, in which no nominally 2+ elements were detected, formed because of the reducing conditions on sintering. The Co, Ni, Cu and Fe have formed metallic alloys. The Mg forms an unidentified Mg-Ti-O phase. No ulvospinel formed. No Zn was detected in the microstructure. Presumably the Zn formed the metal and has volatilised. The system is also deficient in Mn.

#### 4.2.3.2    Nominally 3+ impurities batch (Al, Cr, Mn, Fe, Ga)

The SEM/EDS analysis (Appendix C, fig. C-2/Appendix F, Table F-4) show that this sample consists of:

- pyrochlore
- ~ 30 - 35 vol. % 2M zirconolite
- ~ 30 - 35 vol. % perovskite
- ~ 1 vol. % hibonite
- ~ 1 vol. % of Fe$_3$Ga, which contains ~ 2 wt. % Cr

As with the 4M zirconolite in the 2+ impurities sample above (section 4.2.3.1), the composition of what is believed to be pyrochlore, lies close to the pyrochlore-4M boundary. The pyrochlore has a much different composition (Table F-4) to the pyrochlore in the Ar and air sintered samples. This is probably due to Ti$^{3+}$ formation occasioned by the reducing atmosphere on sintering. Some Fe$_3$Ga forms, so under these conditions the Ga and Al are not exactly equivalent.  Ga and Fe were not detected in the perovskite, zirconolite or pyrochlore. Some Ga is present in the hibonite. Al, Cr and Mn partition into the pyrochlore, zirconolite and perovskite. Mn is enriched in the pyrochlore.

#### 4.2.3.3    Nominally 4+ impurities batch (Zr, Sn, Hf)

The SEM/EDS analysis (Appendix C, fig. C-3/Appendix F, Table F-5) show that this sample consists of

- pyrochlore
- ~ 20 vol. % 2M zirconolite
- ~ 15 vol. % perovskite
- ~ 2 - 3  metallic tin

The hydrogen has evidently reduced the Sn to the metallic state.  Very little Sn, if any, remains in the other phases. The Zr and Hf partition equivalently in the remaining phases. As with the 2+, and 3+ samples above (sections 4.2.3.1 and 4.2.3.2), the main phase, which is believed to be pyrochlore lies close to the pyrochlore-4M zirconolite boundary. The pyrochlore has a different composition (Table F-5) to the pyrochlore in the Ar and air samples. This is probably due to $Ti^{3+}$ formation on sintering under the reducing conditions.

### 4.2.3.4    Nominally 5+ impurities batch (Nb, Ta)

The SEM/EDS analysis (Appendix C, fig. C-4/Appendix F, Table F-6) show that this sample consists of:

- pyrochlore
- 10 – 15 vol. % 2M zirconolite
- ~ 7 vol. % rutile

The Nb and Ta still prefer to enter the pyrochlore. Some Nb and Ta also enter the zirconolite and rutile. The Nb and Ta enter each phase in approximately equal amounts, to each other. The reducing conditions, which will produce $Ti^{3+}$, have resulted in 2M zirconolite formation. No perovskite was detected in this sample. The valencies of the Nb and Ta are not known.

### 4.2.3.5    Nominally 6+ impurities batch (Mo, W)

The SEM/EDS analysis (Appendix C, fig. C-5/Appendix F, Table F-7) show that this sample consists of:

- pyrochlore
- ~ 10 vol. % 2M zirconolite
- ~ 10 vol. % perovskite
- ~ 10 vol. % of metallic (W,Mo) alloys

Most of the W and Mo have formed a metallic alloy and only small amounts, much less than the Ar or air sintered samples, remain in the other phases. Perovskite has formed due to the reducing conditions on sintering

## 4.3  Batches Doped with Glass Formers (Al, B, K, Na, Si)

The densities of the "glass-doped" pellets made to date are given in Table 12.

### 4.3.1  LLNL Glass-doped Batch

Phases detected in the sample sintered at 1250°C (Appendix D, Fig. D-1/Appendix F, Table F-14) were:

- Pyrochlore
- ~ 10 vol. % of a silicate phase, probably a glass
- ~ 10 - 15 vol. % 2M zirconolite
- ~ 7 - 10 vol. % brannerite
- ~ 3 vol. % rutile
- ~ 1 vol. % plagioclase, associated with the glass

Most of the Al is in the silicate glass, with significant amounts taken up by the pyrochlore and zirconolite. Al was also found in all the other phases. The bulk of the Na is in the silicate glass with some of it being in the plagioclase. K was not detected in the crystalline phases or the glass.

Phases detected in the sample sintered at 1300°C (Appendix D, Fig. D-2/Appendix F, Table F-14) were:

- Pyrochlore
- ~ 10 vol. % of a silicate phase, probably a glass
- ~ 10 vol. % 2M zirconolite
- ~ 10 - 15 vol. % brannerite
- ~ 3 vol. % rutile
- ~ 1 vol. % of titanite
- < 1 vol. % plagioclase, associated with the glass

The compositions of the phases in the 1250 and 1350°C samples are similar, with some minor variations.

Phases detected in the sample sintered at 1350°C (Appendix D, Fig. D-3/Appendix F, Table F-14) were:

- Pyrochlore
- ~ 10 vol. % of a silicate phase, probably a glass
- ~ 5 vol. % rutile
- ~ 5 vol. % 2M zirconolite
- ~ 3 - 5 vol. % brannerite

The compositions of the 1350°C sample phases are very similar to the 1300°C sample.

At 1250°C the grain size of the pyrochlore is ~ 2 – 4 μm, by 1300 °C the grain size is ~ 5 – 10 μm and at 1350°C the grain size is similar to the 1300°C sintered sample. Apart from grain growth, the overall look of the pyrochlore grains ("blocky") does not change (figs.

The brannerite grains grow from ~ 5 - 10 µm at 1250°C to 20 – 60 µm at 1300°C, however at 1350°C there is less brannerite and the grain size of this brannerite is reduced to < 5 µm.  Presumably, the brannerite grains have been attacked by the glass.

Small amounts of a plagioclase were detected in the samples fired at 1250 and 1300°C, but not the 1350°C sample. A small amount of titanite (sphene) was detected in the 1300°C sintered sample.

The sample sintered at 1300°C shows signs of partial melting and grain growth compared to the sample sintered at 1250°C. Similar phases are present in both these batches, though the compositions of the phases in the two samples are different (Table F-14). There is less compositional difference between the 1300 and 1350°C samples (Table F-14).

## 4.3.2  LLNL Glass-doped Batch With Additional Al

Phases detected in the sample sintered at 1300°C (Appendix D, Fig. D-4/Appendix F, Table F-15) were:

- Pyrochlore
- ~ 25 vol. % 2M zirconolite
- ~ 5 - 10 vol. % brannerite
- ~ 5 vol. % rutile
- ~ 3 vol. % plagioclase
- ~ 3 vol. % of  what is believed to be magnetoplumbite
- ~ 2 vol. % of a silicate phase, probably a glass

The addition of Al has changed the composition of the microstructure relative to the 1300°C sinter (section 4.3.1, above). There is less silicate phase - the grain size of this silicate phase is too small for accurate compositional analysis (emissions from the surrounding phases are picked up). The phases that form at the expense of the silicate phase are more plagioclase, a magnetoplumbite phase and more 2M zirconolite. The brannerite has a smaller grain size than that in the glass-doped batch sintered at 1300°C (section 4.3.1).

## 4.3.3  LLNL Glass-doped Batch With Additional B

Phases detected in the sample sintered at 1300°C (Appendix D, Fig. D-5/Appendix F, Table F-15) were:

- Pyrochlore
- ~ 10 - 15 vol. % 2M zirconolite
- ~ 5 vol. % brannerite
- ~ 5 vol. % rutile
- ~ 10 - 15 vol. % of a silicate phase, probably a glass

The addition of boron has changed the composition of the microstructure relative to the 1300°C sintered glass (section 4.3.1). There is no plagioclase or titanite and less brannerite. In addition, the grain size of the brannerite is much smaller – closer to that of the 1350°C glass-doped sinter (fig. D-3).

If B and Al were equivalent then this batch and the additional Al batch (section 4.3.2) should be the same. They are not and therefore B and Al are not equivalent in this system.

## 4.3.4  LLNL Glass-doped Batch With Additional Na and K

Phases detected in the sample sintered at 1300°C (Appendix D, Fig. D-6/Appendix F, Table F-15) were:

- Pyrochlore
- ~ 15 - 20 vol % perovskite
- ~ 10 - 15 vol. % 2M zirconolite
- ~ 10 vol. % of a silicate phase, probably a glass

The addition of Na and K has changed the composition of the microstructure relative to the 1300°C sintered glass (section 4.3.1). There is no plagioclase, titanite or brannerite. The Na promotes the formation of a Na-Ce perovskite at the expense of these phases. The silicate phase had much less Ca but more Na and K.  Potassium was only detected in the glass. It appears to be deficient in the sample and is assumed to have volatilised. Na was detected in significant amounts in the perovskite, pyrochlore 2M zirconolite and glass. Therefore, Na and K are not equivalent in this system.

**Table 12 Densities of the glass-doped batches sintered in Ar for 4 hours at 1250 - 1350°C.**

| Pellet No. | Powder No. | Description | Sintering Temperature (°C) | Sintered Density (g/cm$^3$) | Open Porosity(%) |
|---|---|---|---|---|---|
| mws980231 | mws980209 | Glass-doped | 1250 | 4.46 | 3.5 |
| mws980232 | mws980209 | Glass-doped | 1300 | 3.19 | 19.5 |
| mws980338 | mws980209 | Glass-doped | 1350 | 4.42 | |
| mws980388 | mws980368 | Glass-doped + Al | 1300 | 3.12 | 32.0 |
| mws980389 | mws980369 | Glass-doped + B | 1300 | 2.91 | 3.4 |
| mws980390 | mws980370 | Glass-doped + Na & K | 1300 | 4.21 | 2.0 |

## 4.4  Summary of Results

### 4.4.1  Firing Atmosphere Effects

Generally, firing in air produces similar results to firing in Ar, with a few variations; namely, that the pyrochlore fired in air has more Ca in it and there is less likelihood of forming brannerite.

Sintering in hydrogenous atmospheres is not equivalent to Ar or air - phases such as perovskite, tin and metallic alloys form. The composition of the pyrochlores and zirconolites also change.

### 4.4.2  Nominally 2+ Impurity Elements (Mg, Co, Ni, Cu, Zn, Fe, Mn)

Partitioning of the nominally 2+ impurity elements is not exactly uniform. The nominally 2+ impurity elements are preferentially partitioned in the zirconolite (~0.6 formula units) compared to the pyrochlore (0.17 formula units). The presence of excess amounts of the 2+ elements has resulted in the formation of an ulvospinel and some perovskite. There are subtle differences in the partitioning, such as the fact that little, if any, Zn enters the pyrochlore and Mn prefers to partition into the pyrochlore. Despite these variations, we can consider the Co, Ni, Fe, Mn and Mg to be equivalent, as they will all enter the pyrochlore-zirconolite phases. The Zn is only partially equivalent as it may be volatile to some extent, but it can be accommodated into the 2M zirconolite. Cu is also not considered to be equivalent as it appears to be volatile when sintered in Ar. In the air sintered Pu/U-doped sample some Cu was detected in the 2M zirconolite.

The charge compensation for the 2+ elements substituted in the Ti site occurs by rare-earth – actinide substitution in the Ca site of the pyrochlore and zirconolite. A typical baseline formulation has ~ 0.9 – 0.95 formula units of Ca in the pyrochlore[5] and the samples with the 5+ and 6+ elements have 0.93 to 1.0 formula units of Ca. When 2 and 3+ elements are present the Ca is typically in the range 0.79 – 0.86 formula units

### 4.4.3  Nominally 3+ Impurity Elements (Al, Cr, Mn, Fe, Ga, V)

From the above results the Al, Cr, Mn, Fe, Ga and probably the V (if we ignore the fluxing effect) can be considered equivalent. This is because all of these elements can be accommodated into the pyrochlore and zirconolite. In hydrogenous sintering atmospheres the Fe and Ga form $Fe_3Ga$, which contains some Cr, and are therefore not equivalent to the other elements. Al, Mn and Cr are approximately equivalent under these conditions.

The charge compensation mechanisms are broadly similar to those of the 2+ elements.

## 4.4.4  Nominally 4+ Impurity Elements (Zr, Sn, Hf)

Based on these results the Hf and Zr and Sn can be considered equivalent under Ar and air sintering conditions. In hydrogenous atmospheres the Sn is reduced to metal and is not equivalent.

## 4.4.5  Nominally 5+ Impurity Elements (Nb, Ta)

The Nb and Ta enter each phase in approximately equal amounts, hence the Nb and Ta can be considered equivalent. The sintering atmosphere does not affect the equivalence. The Nb and Ta enter the Ti sites in the pyrochlore; charge compensation proceeds by forcing the trivalent rare earths from the Ca to the Zr-Hf site in the pyrochlore. This can be seen in the increase in Ca in the pyrochlore, particularly in the Pu-doped samples (Table F-11). In the Ce-doped samples some charge compensation may also occur by the reduction of Ce from $Ce^{4+}$ to $Ce^{3+}$ if sintered under sufficiently reducing conditions.

## 4.4.6  Nominally 6+ Impurity Elements (Mo, W)

Based on the above results, the W and Mo can be closely considered equivalent. The charge compensation mechanisms are broadly similar to those of the 5+ elements.

## 4.4.7  Th/Np-doped Batch

The Th and Np do not behave exactly equivalently in that the Th tends to be enriched in the brannerite phase and deficient in the pyrochlore, relative to the Np. The Th and Np do partition equivalently in the actinide/rare earth oxide that formed. Since significant amounts of Np and Th can be incorporated into the brannerite and pyrochlore phases, we believe that Np and Th can be considered equivalent for the purposes of this project.

## 4.4.8  Glass-forming Elements

The Al and B are not equivalent. The Al tends to result in zirconolite formation, whereas the B is believed to remain in the glass. As found in last year's work [5], we believe that the Na and K may be volatile, or partially volatile. Na can be accommodated in the zirconolite and pyrochlore. If sufficient quantities are present, Na will promote the formation of a Na-rare-earth perovskite. Na can also be found in the plagioclase and the silicate phase. K was only found in the silicate phase of the sample made with additional Na and K. Therefore, Na and K are not considered equivalent.